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Effects of strain gradient on charge offsets and pyroelectric properties of ferroelectric thin films

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The Landau-Ginzburg-Devonshire theory is used to study the effects of the strain gradient due to the epitaxial stresses in ferroelectric thin films sandwiched between two different substrates. The polarization in the film is found to be nonuniform, resulting in charge offsets and an asymmetric hysteresis response with characteristics similar to those in compositionally graded ferroelectric materials. The authors' results suggest that the charge offset and pyroelectric effects can also be produced with effect of the strain gradient in film. In addition, such effects are found to be sensitive to an applied load. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2335369]

Functionally graded ferroelectrics in the form of either bulk or thin films possess properties[1–8] different from those of homogeneous ferroelectrics. The distribution of the polarization in graded ferroelectric devices is asymmetric and graded, and there is a translation of the hysteresis loop along the polarization axis with an attendant charge offset. As a result of this asymmetry, other properties such as the effective pyroelectric response, temperature dependence of the dielectric behavior, etc.,[1,3] are also affected.

At the same time, a strain gradient in a uniform ferroelectric thin film may also produce similar effects.[9–14] In this letter, we report on our investigation of the effects of the strain gradient caused by the epitaxial stresses in ferroelectric thin films (FTFs) sandwiched between two different substrates. Following the Landau-Ginzburg-Devonshire (LGD) theory, a general model that includes effects of flexoelectricity and stress gradient is formulated and applied.

The thickness of the FTF is L, and the thicknesses of the rigid substrates are assumed to be much larger than L, so that the system can be considered to remain flat. The polarization P due to the eigenstrain of the ferroelectric transformation (simply called *self-polarization*) is assumed to be perpendicular to the film surface and is homogeneous on the x-y plane. Using the LGD theory and the Legendre transformation, the total free energy per unit area of the film can be written as:[4,9,10,15]

$$\tilde{G} = \int_0^L \left\{ \frac{1}{2}A(T-T_{c0})P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \frac{1}{2}D\left(\frac{dP}{dz}\right)^2 + \frac{1}{s_{11}+s_{12}}\left[2F\left(\frac{\partial u}{\partial z}\right)^2 - 2\gamma P\frac{\partial u}{\partial z} - 2\eta u\frac{\partial P}{\partial z} - 2u\cdot x_0 + x_0^2 + u^2\right] - \frac{1}{2}E_dP - E_{\text{ext}}P \right\} dz + \frac{D}{2\delta_0}P_0^2 + \frac{D}{2\delta_L}P_L^2, \quad (1)$$

where A, B, and C are the expansion coefficients of the Landau free energy and D can be approximated as $\xi^2\cdot|A(T-T_{c0})|$, where T_{c0} is the Curie-Weiss temperature of the bulk material and ξ is the characteristic length along which the polarization varies.[1] γ and η are the direct and converse flexoelectric coefficients, respectively.[9,10] Q_{12} is the electrostrictive coefficient describing the coupling between the mechanical deformation and the self-polarization. P_0 and P_L are the polarizations, and δ_0 and δ_L are the extrapolation lengths at the upper and lower surfaces, respectively. s_{ij} is the elastic compliance tensor. $E_d(z)$ is the depolarization field and $E_{\text{ext}}(z)$ is the external field, which have been defined in Refs. 1, 3, and 4. u is the total biaxial in-plane residual strain in the thin film. $x_1=x_2=x_0$ is the transformation strain given by $x_0=Q_{12}P$.[2] To focus on the effect of the strain gradient, we consider the case for which the combined effects of the depolarization and external fields can be neglected.

The components of the biaxial in-plane residual strain in the thin film can be written as $\varepsilon_1^1(z)=\varepsilon_2^1(z)=u_1(z)$ and $\varepsilon_1^2(z)=\varepsilon_2^2(z)=u_2(z)$. They are produced by the mismatch between the film and the substrates and are functions of the film thickness L and the depth z. If the stress relaxation due to the misfit dislocations is negligible, the strain profile can be written as $\partial u_1/\partial z=-u_{10}/\alpha_2$ and $\partial u_2/\partial z=-u_{20}/\alpha_2$.[9,11] In this letter, the misfit dislocations are assumed to provide the main relaxation mechanism, and the strain profiles as a function of z are given by

$$u_1(L-z,L) = u_{10}\left[\cosh\frac{L-z}{\alpha_1} - \tanh\frac{L}{\alpha_1}\sinh\frac{L-z}{\alpha_1}\right],$$
$$u_2(z,L) = u_{20}\left[\cosh\frac{z}{\alpha_2} - \tanh\frac{L}{\alpha_2}\sinh\frac{z}{\alpha_2}\right], \quad (2)$$

where α_1 and α_2 are decline parameters that measure the penetration depth of the strain. u_{10} and u_{20} are the strains at the upper and lower film-substrate interfaces, respectively.[9,11,12]

Minimization of the total free energy F in Eq. (1) with respect to P and u gives the stationary values of P away from

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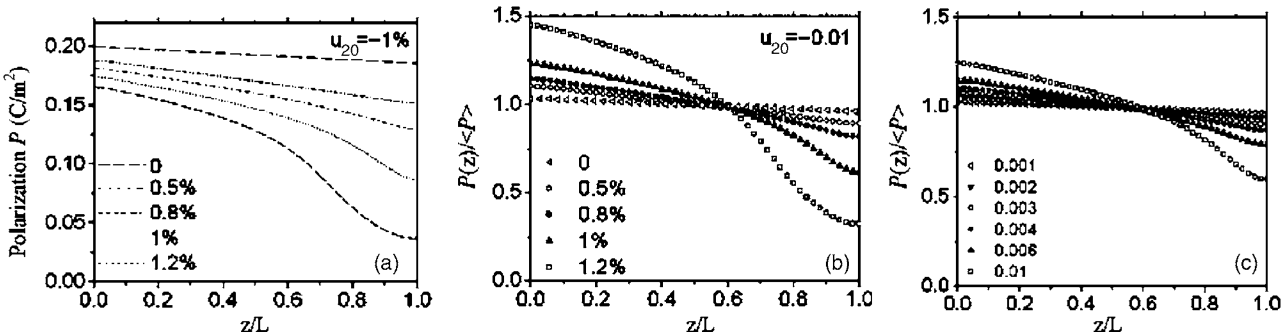

FIG. 1. (a) Polarization profile of the BT thin film sandwiched between lower $SrTiO_3$ CS ($u_{20}=-1\%$) and upper TS ($u_{10}=0\%-1.2\%$) at room temperature. (b) Normalized polarization profiles of BT ferroelectric thin film sandwiched between lower $SrTiO_3$ CS ($u_{20}=-1\%$) and upper TS ($u_{10}=0\%-1.2\%$) at room temperature. (c) Normalized polarization profiles of BT ferroelectric thin film sandwiched between "top-bottom" substrates with an external load at room temperature, where $u_{20}=-u_{10}=0.1\%-1\%$.

the transition points,[9,10,15] i.e., dynamically stable ones, in the following equation:

$$A^*P + B^*P^3 + CP^5 - D^*\frac{d^2P}{dz^2} - \frac{2(\gamma-\eta)}{s_{11}+s_{12}}\frac{d(u_1(z)+u_2(z))}{dz} = 0, \quad (3)$$

where

$$A^* = A(T - T_{c0}) - \frac{4Q_{12}(u_1(z)+u_2(z))}{s_{11}+s_{12}},$$

$$B^* = B + \frac{4Q_{12}^2}{s_{11}+s_{12}}, \quad D^* = D - \frac{2(\gamma-\eta)^2}{s_{11}+s_{12}}.$$

In the present analysis, the boundary conditions on the upper and lower surfaces are assumed to be given by $\partial P/\partial z=0$ at $z=0$ and $z=L$, corresponding to a complete compensation of charges near the ferroelectric and the substrates, with extrapolation lengths $\delta_0=\delta_L\to\infty$.[1,3] Without this assumption, Eq. (3) must yield $\partial P/\partial z=P_0/\delta_0$ and $\partial P/\partial z=P_L/\delta_L$ at $z=0$ and $z=L$.[16]

Results of the polarization distribution along the z direction can be used to calculate the charge offset per unit area ΔQ according to the one-dimensional Poisson's equation,[17]

$$\Delta Q = \frac{1}{L}\int_0^L z\cdot\left(\frac{dP(z)}{dz}\right)\cdot dz. \quad (4)$$

The charge offset has a strong temperature dependence, which has been confirmed both theoretically and experimentally.[1] This is described by an effective pyroelectric coefficient that can be defined as

$$p_{\mathrm{eff}} = \frac{d\Delta Q}{dT} = \frac{1}{L}\frac{d}{dT}\int_0^L z\cdot\left(\frac{dP(z)}{dz}\right)\cdot dz. \quad (5)$$

Since a ferroelectric hysteresis loop can be observed by a Sawyer-Tower circuit, Eqs. (4) and (5) can be rewritten as $\Delta Q=C_Q/LC_F\int_0^L z(dP(z)/dz)dz$ and $p_{\mathrm{eff}}=d\Delta Q/dT=C_Q/LC_F d[\int_0^L z(dP(z)/dz)dz]/dT$, where C_Q is the load capacitance in the Sawyer-Tower circuit and C_F is the capacitance of the ferroelectric.[1]

The main aim of this letter is to investigate the effects on the properties of a ferroelectric thin film produced by a strain gradient due to the difference in the epitaxial stresses produced by different substrates. The widened possibilities suggested by this generalized mechanical boundary condition in functional performance and control, in addition, may prove useful for materials design purposes. In connection, one may choose typical ferroelectric films, such as $PbTiO_3$, $BaTiO_3$ (BT), or $Ba_{0.5}Sr_{0.5}TiO_3$, etc., to be sandwiched between compressive (CS) and tensile (TS) substrates: $LaAlO_3$, $SrLaAlO_4$, $(LaAlO_3)_{0.3}(Sr_2LaTaO_6)_{0.7}$, $SrRuO_3$, $SrTiO_3$, and $KTaO_3$.[16] The mismatch between films and compressive or tensile substrates ranges from about −3% to 2%. However, to remain focused at establishing the principle in this work, we only consider BT films sandwiched between a variety of tensile upper TS and the compressive lower $SrTiO_3$ CS.

The material constants are given in Refs. 4, 13, 15, and 18. By numerically solving Eq. (3), the polarization profile along the z direction can be obtained. According to Refs. 9 and 12, we use values of 100 nm for α_1 and α_2, and L, the thickness of the film. With a correlation coefficient D^* of the order of $\sim 10^{-9}$ (SI units),[9,19,20] the value of the flexoelectric coefficient is $(\gamma-\eta)=0.1\times10^{-9}$ m^3 C^{-1}. We note that parameters for the penetration depth of the strain (α_1 and α_2) are very important for the polarization profiles in ferroelectric thin films, through which properties of the thin film may then be controlled experimentally.

The results for the $TS/BaTiO_3/SrTiO_3$ ($u_{10}=0\%-1.2\%$ and $u_{20}=-1\%$) system at room temperature (30 °C) are shown in Fig. 1(a), where $u_{10}=0$ means that the top face of BT film is free. The effects of the strain gradient on the polarization profile due to the substrates are obvious. For comparison,[1] the polarization profiles of Fig. 1(a) are normalized and presented in Fig. 1(b). It can be seen that our results are similar to those due to compositionally graded ferroelectric film,[1] but with effects that are about an order of magnitude larger.

An external load on the substrates leads to changes in the strain gradient through u_{10} and u_{20}, resulting in corresponding changes of the polarization profile of the film. To estimate this effect, we also calculate the polarization profiles for cases in which $u_{20}=-u_{10}=0.1\%-1\%$. The results are shown in Fig. 1(c). Comparison of Figs. 1(b) and 1(c) shows that the change of both the stress and the stress ratio significantly affects the distribution of the polarization, and hence the charge offset.

Using Eqs. (4) and (5), the charge offset per unit area and the effective pyroelectric coefficient as a function of temperature can be calculated. Figure 2(a) shows the charge offset as a function of temperature for a compressive lower $SrTiO_3$ substrate and various tensile upper substrates. It is

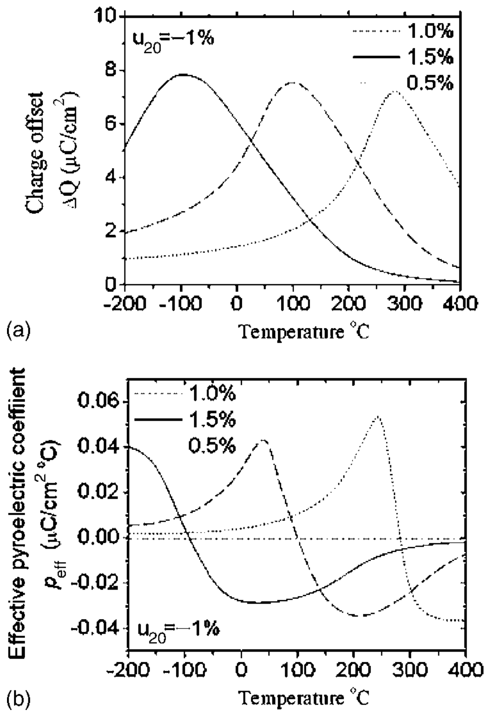

FIG. 2. (a) Charge offset per unit area ΔQ and (b) effective pyroelectric coefficient p_{eff} as a function of temperature in $BaTiO_3$ sandwiched between "top-bottom" substrates, where $u_{20}=-1\%$ and $u_{10}=0.5\%$, 1%, and 1.5%.

interesting that the charge offset is very sensitive to changes in the residual strain. Moreover, Fig. 2(a) shows that the charge offset increases with temperature below T_{ch} and decreases with increasing temperature above T_{ch}. We note that $T_{\mathrm{ch}}=-103$ °C for $u_{20}=1.5\%$, 98 °C for $u_{20}=1\%$, and 310 °C for $u_{20}=0.5\%$. This behavior is explained by the increased self-polarization at lower temperatures. Competing with the effects of the strain gradient, the increased polarization tends to reduce the charge offset by keeping the polarization profile constant along the z direction. At higher temperatures the charge offset also decreases with increasing temperature as the self-polarization decreases. The effective pyroelectric coefficient as a function of temperature is shown in Fig. 2(b). The effects of the strain gradient are obvious.

In summary, based on a thermodynamic approach using the Landau-Ginsburg-Davenshire formulation, a general model for ferroelectric thin films including effects of flexoelectricity is formulated. This model is used to study the effects of the strain gradient due to the epitaxial stresses in ferroelectric thin films sandwiched between two different substrates. Our results show that the properties of ferroelectric thin films can be controlled for design purposes if we choose the appropriate substrates. Moreover, our results indicate that the residual stress gradient, which is induced by the epitaxial stresses or other reasons, may play an important role in the properties of ferroelectric thin films, such as distribution of the polarization, the charge offset, pyroelectric coefficients, etc.

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